

Republic of Iraq
Ministry of Higher Education and Scientific Research
University of Babylon
College of Education and pure Science



Theoretical study of structural and electronic properties of PVA/ Al_2O_3 nanocomposite by using Density Functional Theory

A Thesis Submitted to the council of college of Education and pure Science, Babylon University as partial Fulfillment of the Requirement of the Degree Higher Diploma Education /Physics of Materials and its Applications.

By

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2021 A.D.

1443 A.H.

بِسْمِ اللَّهِ الرَّحْمَنِ الرَّحِيمِ

((يَا أَيُّهَا الَّذِينَ آمَنُوا إِذَا قِيلَ لَكُمْ تَفَسَّحُوا فِي الْمَجَالِسِ فَافْسَحُوا يَفْسَحِ اللَّهُ
لَكُمْ ۗ وَإِذَا قِيلَ انشُرُوا فَانشُرُوا يَرْفَعِ اللَّهُ الَّذِينَ آمَنُوا مِنْكُمْ وَالَّذِينَ أُوتُوا
الْعِلْمَ دَرَجَاتٍ ۗ وَاللَّهُ بِمَا تَعْمَلُونَ خَبِيرٌ))

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We certify that we have read this thesis entitled " **Theoretical study of structural and electronic properties of PVA/Al₂ O₃ nanocomposite by using Density Functional Theory**" and in our opinion as an examining committee examined the student (**Dohaa Neamah Selbi Hadi**) in the contents ,it is adequate with (**Asst .Prof .Dr . Hind Ahmed Mohammed Roof**) as a thesis meets the standard Higher Diploma Education / Physics of Materials and its Applications.

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Dedication

It is genuine gratitude and warm regard that I dedicate this work to my family, Friends and teachers. And a special dedication is for Iraqi martyrs of wars and attacks.

DOHAA

ACKNOWLEDGMENT

To begin with , many thanks to Allah for inspiring us to reach toward knowledge, and peace upon the Messenger Mohammed and his family. I would like express my kind thanks and appreciation to the respected supervisor for suggesting the research and her support, guidance and encouragement throughout the duration of this research project my thesis , help and follow up throughout the stages.

DOHAA

Abstract

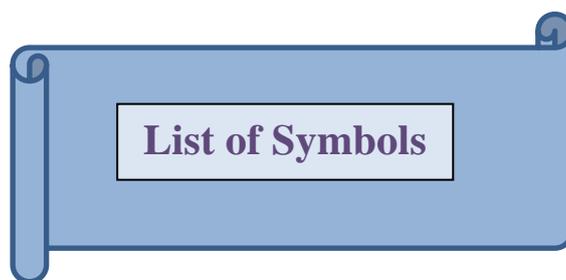
The effect of addition the (Al_2O_3) nanoparticle size on the geometric , electronic and spectral properties of the polymer (PVA) (43 Atom) is study by Gaussian 0.9 program with help of Gaussian View 0.5 using density function theory (DFT) with local spin density approximation (LSDA) and *LanL2DZ* basis sets. The geometric properties included improving geometric optimization (bonds and angles). As for the electronic properties included the (Ionization potential ,Electron affinity, Chemical hardness ,Chemical softness, Electronegativity, Total energy, energy gap, Electrophilicity and density of states) as well as spectral properties, which included (Infrared (IR), Raman , Ultraviolet (UV)-Visible and Nuclear magnetic resonance (NMR)). The results showed that adding (Al_2O_3) nanoparticles had a direct effect on all the properties of the studied structure. Where adding (Al_2O_3) nanoparticles lead to decrease the energy gap from (6.856 eV) to (3.483 eV) .the same applies to the average binding energy , where a decrease in its values was observed with the increase in the number of atoms of the nanocomposites studied. A small energy gap means small excitation energies to the manifold of excited states. Therefore, soft molecules with small energy gaps, their electron density change more easily than a hard molecule, and due to that, soft molecules will be more reactive than hard molecules.

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List of Symbols

Symbol	Description
PVA	Polyvinyl Alcohol
Al_2O_3	Oxide aluminium
R	Electrical Resistance
A	Area
w	Angular Frequency
K_B	Boltzman Constant
D	Dispersion Factor
E	Electrical Field Intensity
UV	Ultraviolet Spectrum
\hbar	The Reduced Planck Constant
∇^2	The laplacian Operator
$V(r, t)$	potential Energy
\hat{H}	The Hamiltonian Operator
$\psi(\vec{r}, \vec{R})$	The Total Wave Function
E_{tot}	The Total Energy
m_e	Electronic Mass
\hat{T}_e	The Electronic Kinetic Energy Operator
\hat{T}_n	The Nuclear Kinetic Energy Operator
\hat{V}_{ne}	The Attractive Interactions between Nuclei and Electrons Operator
\hat{V}_{ee}	The Repulsive Electron– Electron Interactions Operator

\hat{V}_{nn}	The Repulsive Nucleus- Nucleus Interactions Operator
$Z_{A,B}$	The Atomic Number of Atoms A and B
m_A	The Mass of Atom A
r_{AB}	The Distance between Nuclei A and B
r_{iA}	The Distance between Nucleus A and Electron i
r_{ij}	The Distance between Electrons i and j
E_e	The Electronic Energy
E_{nuc}	The Constant Nuclear Repulsion
E_0	The Ground-State Energy
Φ	The Trial Function
N	The Number of Electrons
$\rho(r)$	Electron Density
E_{HOMO}	Energy of the Highest Occupied Molecular Orbital
E_{LUMO}	Energy of the Lowest Unoccupied Molecular Orbital
E_g	Energy Gap
K	Chemical Potential
X	Electronegativity
η	Chemical Hardness
S	Chemical Softness
DFT	Density Functional Theory

HF	Hartree–Fock
NMR	Nuclear Magnetic Resonance
IR	Infrared Ray
UV	Ultra-Violet
UV-Vis	Ultraviolet-Visible
MOs	Molecular Orbitals
SCF	Self-Consistent Field
LCAOs-MO	Linear Combination of Atomic Orbitals- Molecular Orbital
LSDA	Local Spin Density Approximation
G09	Gaussian 09
GV5	Gauss view 5.0.8
HOMO	Highest Occupied Molecular Orbital
LUMO	Lowest Unoccupied Molecular Orbital
ESP	Electrostatic Potential
IP	Ionization Potential
EA	Electron Affinity
k	Extinction coefficient

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CHAPTER ONE

INTRODUCTION

1.1 Introduction

Nanotechnology is a field of applied science and technology that deals with materials in the nanoscale range with large surface areas [1]. It is the application of science and technology to manipulate the matter at atomic and molecular scale. It has the ability to build micro and macro materials and products with atomic precision [2]. Nanoparticles have attracted considerable interest recently in the field of food, agriculture and pharmaceutical [3]. Nanotechnology is not new to polymer science as prior studies before the age of nanotechnology involved nanoscale dimensions but were not specifically referred to as nanotechnology until recently [4].

1.2 Polymer Nanocomposites

Polymer nanocomposites have polymer matrix reinforced with nanosized phase (nanofillers) such as nanoparticles, nanotubes, nanosheets, and nanofibers....etc. The physical properties of these composites mainly depend on the interaction between nanofillers and polymer molecules [5]. Nowadays, studies on polymer nanocomposites have attracted much attention in view of their wide range of applications in the field of polymer nanotechnology. The polymer nanocomposites heavily rely on geometry, size distribution, aggregation and surface chemistry of organic/inorganic nanoparticles as well as matrix–nanoparticle interactions. Nevertheless, the properties of nanocomposites were found to depend on the type of nanoparticles, the

content of nanofillers and nature to bridge chemically and physically with the polymer matrix [6]. Nanocomposites are as multiphase materials, where one of the phases has nanoscale additives [7]. The conventional classification of materials as metal, semiconductor and insulator, then we can have composites of metal–semiconductor, metal–insulator, semiconductor–insulator. Nanocomposites of organic and inorganic materials can possess advantages of both organic polymers (dielectric, ductility, flexibility) and inorganic materials (high thermal stability, rigidity, strength, high refractive index, hardness), thus have many applications[8]. Developing nanocomposites could be a solution to adjust the properties of individual nanomaterials appropriately. In particular, in the field of semiconductor materials, nanocomposites composed of two or more materials are widely used to alter their electronic and optical properties [9].

1.3 Poly (Vinyl Alcohol) (PVA)

Poly (vinyl alcohol) (PVA) has attracted the attention of many researchers in the reason of their interesting properties such as high dielectric strength, good charge storage capacity, commercial availability, low cost, good mechanical and optical properties[10]. PVA present an excellent host material due to its good film morphology, combined with high flexibility. However, these properties are highly susceptible on humidity which reduces the durability and stability of such polymer; it has been mainly used as a dielectric material, membrane, or adhesive

because of its high solubility in water [11]. PVA is a non-toxic, biocompatible synthetic polymer, having good transparency, high dielectric strength, and fast charge transfer at electrode-nanocomposite interface [12]. Poly (vinyl alcohol) (PVA) is one type of hydrophilic polymer. It's can be mixed with other materials to get a better composite according to its usefulness [13]. The significant feature of PVA is semi crystalline nature that is the presence of both crystalline and amorphous regions causing crystal-amorphous interfacial effects which increases the physical properties [14]. PVA has a carbon chain backbone with hydroxyl groups attached to methane carbon, Figure (1.1) .

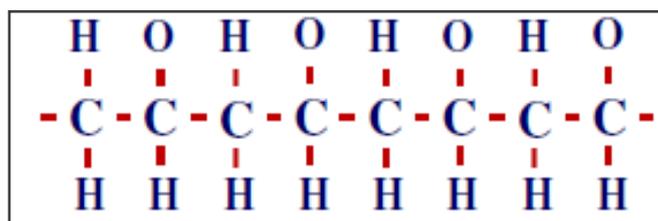


Fig. (1.1). The structure of Poly (vinyl alcohol) [15]

These OH groups can be a source of hydrogen bonding, assist the formation of polymer electrolytes and plays an important role in determining the chemical and physical properties of PVA [16]. The action between the nanoparticles dispersing in the PVA matrix so, the Fourier-transform infrared (FTIR) spectra exhibit irregular shifts related to corresponding bands with change in intensities of pure PVA . the irregular shifts indicated in the spectrum are mainly because of orderly arranged hydroxyl groups of the polyvinyl alcohol chain accomplished by

forming stable complex compounds or else bonding with certain substances, as in Figure (1.2).

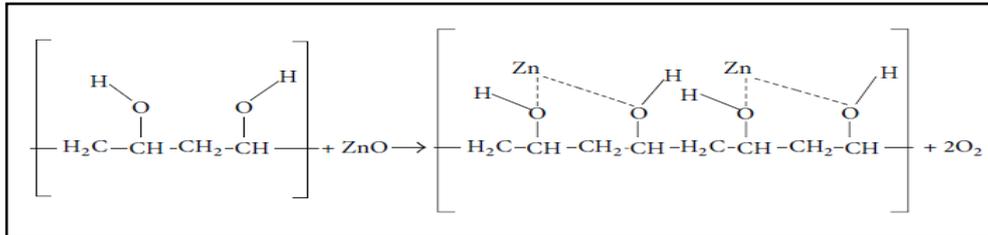


Fig. (1.2). Possible chemical interaction between PVA/ZnO polymer nanocomposites [14].

1.4 Aluminium oxide Al_2O_3 (Alumina)

Alumina is a ionic-covalent solid that does not yield under load as metals and alloys do. The strong chemical bonds as shown in Figure() in alumina are the roots of several of its characteristics such as the low electric and thermal conductivity, the high melting point that makes it practically impossible to shape alumina by casting, and the high hardness that characterizes this material and makes its machining complex and costly. The brittleness of alumina is the main concern of engineers while designing alumina components. In metals, crack energy is dissipated by yielding at the crack tip, while alumina components may fail without any previous plastic deformation at the location of high tensile stresses, such as surface defects, notches, internal flaws, or on the occurrence of thermal shocks[17]. Al_2O_3 is an advanced ceramic material with wide applications in the structural, electrical, automotive, and electronic fields. alumina is known to exist in a number of metastable polymorphs in addition to the thermodynamically stable $\alpha-Al_2O_3$ [18]. The phase of alumina ($\alpha-Al_2O_3$),

which has a broad bandgap (8.7 eV), is widely used in optical devices. The hexagonal structure of α - Al_2O_3 is built up by close-packed planes of oxygen and aluminum ions with one third of the Al sites being empty. The base structure for doping is presented in Figure (1.3)[19].

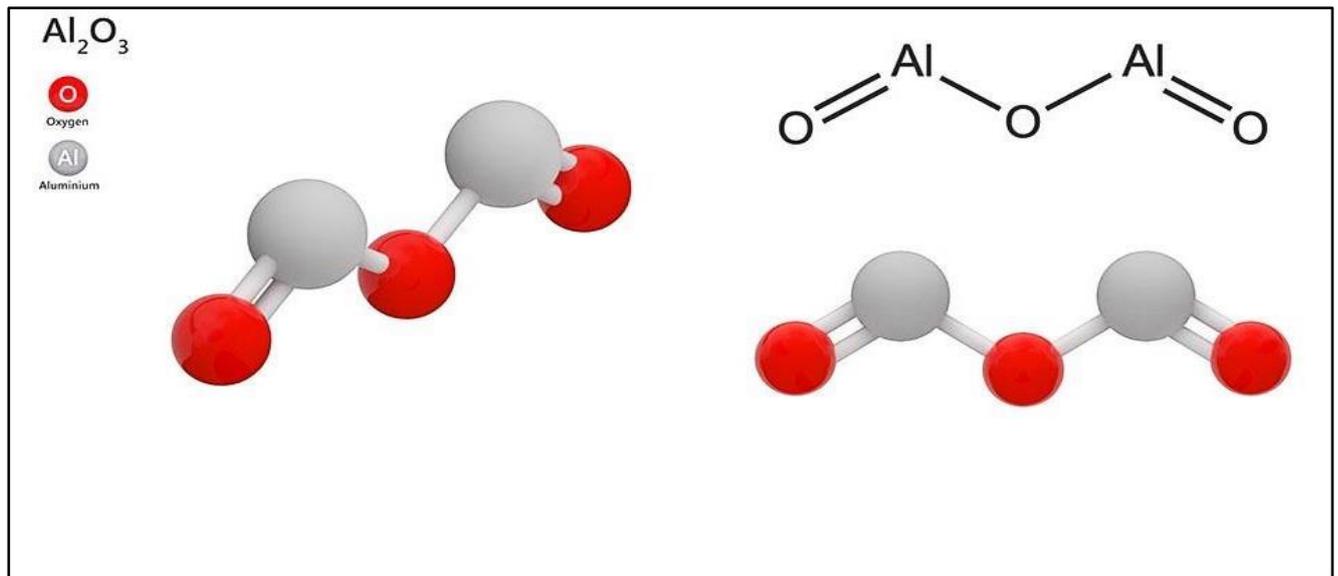


Fig. (1.3). Structure of Al_2O_3 : red, O atoms; purple, Al atoms; yellow, O vacancy; and green, doping site.

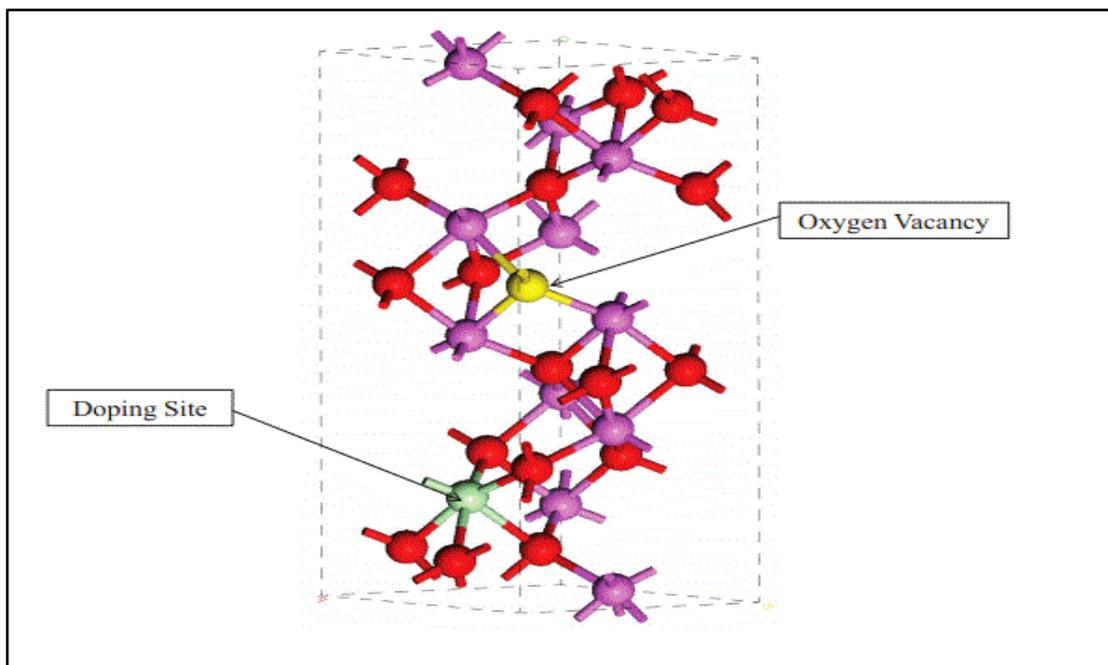


Fig. (1.4). Structure of α -Al₂O₃: red, O atoms; purple, Al atoms; yellow, O vacancy; and green, doping site.

1.5 Literature Survey

1- Ma, H., Shi, T., & Song, Q . [20] in (2014) were prepared PVA/SiO₂-TiO₂ hybrid fibers by sol-gel dip-coating method. PVA and SiO₂-TiO₂ were linked through chemical bond in the hybrid fiber, and forms a homogeneous system. There was a comparing with pure PVA fiber, They found that the crystallinity of hybrid fibers decreased dramatically and the hybrid fibers shield the ultraviolet rays effectively by adding TiO₂, and this could slow the elderly process of the PVA/SiO₂ hybrid materials,

and too the thermal resistance of hybrid fiber is better than pure PVA fiber. The resulting PVA/SiO₂-TiO₂ hybrid materials might be very promising for use in ultraviolet radiation shield fibers due to the ultraviolet radiation shield effect of TiO₂.

2- Goswami, R., Pande, C.,S., Bernstein, N., Johannes, M.D., Baker, C., & Villalobes, G. [21] in (2015) were reported an order of magnitude enhancement of strength of sputter deposited Al/Al₂O₃ multilayers After annealing. Also examine the fracture behavior of the post annealed Al/Al₂O₃ multilayered composites with TEM and density functional theory (DFT) simulations. DFT showed that the multilayers are not likely to delaminate at the Al/Al₂O₃ interface, consistent with the experimental observations.

3- Jiande, Gu., wang, J., & Leszczynski, J. [22] in (2018) were examined, and suggested a new surface model of γ -alumina . The local structure of this new surface of γ -alumina has been optimized by the density functionals along with the full electron basis sets by using periodic boundary condition. The singly occupied MO on Al(I) might be the key component for the catalytic activities of the γ -alumina.

4- Samanta, P.N.,& Leszczynski, J. [23] in (2018) Were studied the thermoelectric transport properties of metal-ceramic interface based on Al and γ -Al₂O₃ are explored by employing the non-equilibrium Green's function formalism (NEGF) coupled with density functional theory (DFT).

Several interfacial electronic properties such as charge transfer, potential barrier, and atomic orbital overlap are critically analyzed based on the DFT derived results of electrostatic difference potential, electron density difference, and the spin-polarized density of states in the fully relaxed structure of the interface.

5- Batchu, S. p., Wang, H.L, Chen, W., Zheng, W., Caratzoulas, S., Lobo, R.T., & Vlachos, D.G . [24] in (2021) Were used Density-functional Theory calculations and kinetic analysis investigate the efficiency of Ga-modified γ -Al₂O₃ (110) surfaces for the catalytic dehydrogenation of ethane and elucidate the synergy between Ga and Al sites. They found that grafted Ga sites are catalytically inactive. In contrast, Ga-doped sites exhibit 5-fold enhancement in catalytic activity when compared to the sites on pristine Al₂O₃, owed to the synergy between neighboring Al_{III} and Ga_{IV} sites.

1.6 The Aims of Project

In this research we study the new types of (PVA-Al₂O₃) nanocomposite that it used in a wide variety of biomedical and industrial applications and compute the structural ,electronic and spectral properties of (PVA-Al₂O₃) nanocomposite . The results of the properties of singly occupied MO on (PVA-Al₂O₃) showed that can be the key component for the catalytic activities of the alumina .

CHAPTER TWO

THEORETICAL PART

2.1 Introduction

There is increasing research in nanocomposites owing to improvements in, optical, electrical, mechanical properties. Nanoparticles represent as advanced technological materials because of their attractive electrical/electronic properties and high refractive index[25, 26].

This chapter contains a theoretical part which effort on the theories of structural and electronic properties.

2.2 Computational Chemistry

Computational chemistry is a set of techniques used to investigate chemical matters by using a computer. Computational chemistry can create (predict, for new and unknown compounds) molecular energy and geometry optimization, energy and spatial structure of transition states, bond energy, reaction energy, molecular orbits, dipole moment (polarity), atomic charges, polarization, properties of spectroscopy of Raman and IR, vibration frequencies, characteristics of thermal chemistry and reaction method[27].

2.3 Methods of Computational Chemistry

There are many methods used in computational chemistry. Some of these methods depend on the complete solution of theories and equations. Others rely on the integration of theoretical and practical calculations. They also depend on the theories of quantum mechanics, while others rely on classical mechanics, and basic methods used in computational chemistry are:

2.3 .1 Molecular Mechanics Methods

These methods are one of the simplest and fastest methods, but in contrast provide less accurate results than quantum mechanics methods. Their importance appears in their speed and is used for relatively large structures such as proteins, steroids, etc. These methods, represent the molecules as it is a group of balls connected to each other by the springs. Thus, when the normal (stable) length between two atoms and the value of the angle and the energy needed for the tensile or the bending of this bond is known, the energy of this group of springs and balls can be calculated, in other words, the spatial structure is changed in order to obtain the least possible energy as Figure (2.1).

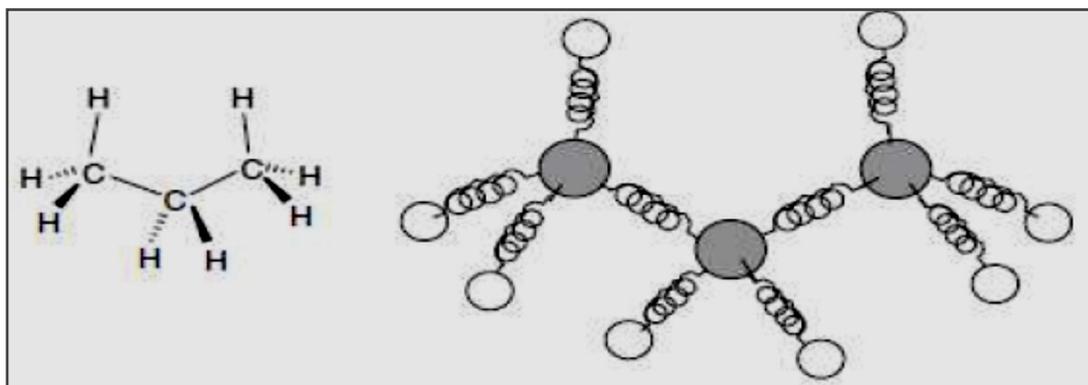


Fig. (2.1). Expressing molecules a group of balls connected by the springs[28].

The disadvantages of this method that neglects study of electrons so they cannot know the properties of reactions related to electrons such as the charge of atoms, dipole moment and other properties[29]. The energy of the molecule (in these methods) is the sum of the energy of the bond and the non-bonding.

The energy of the bond is the energy produced by the direct effect by bonding such as the energy of the bond (the tensile energy), the angular energy and the energy of the twisting links). As for the another energy, it is the static as forces of Vander Waals. The molecule's energy can be expressed mathematically:

$$E = E_{\text{Bond}} + E_{\text{Non bond}} \quad \text{.....(2-1)}$$

$$E = \sum_{\text{Bond}} E_{\text{Stretch}} + \sum_{\text{Angles}} E_{\text{bend}} + \sum_{\text{Dihedrals}} E_{\text{Torsion}} + \sum_{\text{Pairs}} E_{\text{Non bond}} \quad \text{.....(2-2)}$$

Molecular mechanics differ in fields of force. A force field is a set of parameters and equations that describe atoms and their relationship (describing the types of interaction between atoms). Many of these methods have been developed, and the difference between them is the shape of function that specific for energy and the basic parameters used. These methods are designed to be more suitable for use in a range of compounds than others[30].

2.3 .2 *Ab Initio*

It's a Latin word meaning (from the beginning). This is the basis of this group. It is based on the Schrodinger equation, which is based entirely on the theories of quantum mechanics and its solutions from zero. This equation (Schrodinger equation) describes the movement of the electron within the molecule and when solved, we get energy and a wave function. The resultant wave function is a mathematical equation that

expresses the electronic distribution of electrons in the molecule. By knowing this distribution, the polarity of the molecule can be calculated. It can also calculate molecular spatial structure, vibrational energy, ionization energy, electronic affinity, dipole moment and other characteristics [31]. Schrodinger's equation is the nucleus or building block of quantum physics and thus of chemistry theory and arithmetic, written by the Erwin Schrodinger in 1925 and published in 1926. From during which it was the first description of the electron as a wave state [28]:

$$\hat{H}\psi(\vec{r}, t) = E\psi(\vec{r}, t) \quad \dots\dots(2-3)$$

Where \hat{H} the Hamiltonian operator, Ψ the total wave function of the molecular system, E the energy.

The developed expression of the Hamiltonian operator is:

$$\hat{H}_{\text{total}} = \hat{T}_{\text{elec.}} + \hat{T}_{\text{nucl.}} + \hat{V}_{\text{nucl. elec.}} + \hat{V}_{\text{elec. elec.}} + \hat{V}_{\text{nucl. nucl.}} \quad \dots\dots(2-4)$$

Where \hat{T}_e and \hat{T}_n are the kinetic energy operators of the electrons and nuclei, respectively. \hat{V}_{ne} the Coulomb attraction between the nuclei and electrons, (\hat{V}_{ee}) the Coulomb repulsion between electrons, \hat{V}_{nn} the Coulomb repulsion between nuclei. The kinetic energy operators are represented as:

$$\hat{T}_e = - \frac{\hbar^2}{2m_e} \sum_i \nabla_i^2 \quad \dots\dots(2-5)$$

$$\hat{T}_n = - \frac{\hbar^2}{2M_A} \sum_A \nabla_A^2 \quad \dots\dots(2-6)$$

Where m_e and M_A are the electron and nuclear mass, respectively, ∇_i^2 is the Laplacian operator of i electrons, which in Cartesian coordinates has

the form:

$$\nabla_i^2 = \frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2} \quad \dots\dots\dots(2-7)$$

The potential energy operators are represented as:

$$\hat{V}_{nn} = \sum_{A < B} Z_A Z_B \frac{e^2}{R_{AB}} \quad \dots\dots\dots(2-8)$$

$$\hat{V}_{ne} = - \sum_A \sum_i Z_A \frac{e^2}{r_{Ai}} \quad \dots\dots\dots(2-9)$$

$$\hat{V}_{ee} = \sum_{i < j} \frac{e^2}{r_{ij}} \quad \dots\dots\dots(2-10)$$

Where $r_{ij} = |\vec{r}_i - \vec{r}_j|$ and Z_A is the charge of nuclei A, r_{Ai} is the distance between nucleus and electron, r_{ij} is the distance between i electron and j electron and R_{AB} is the distance between A nucleus and B nucleus. Schrodinger equation is known as an equation is not solvable except for single-electron systems such as hydrogen. Therefore, it is necessary to provide some mathematical approximations to solve this equation and from the simplest of these approximations approximation Hartree-Fock where this approximation depends on the principle of the central field. This means that the Coulombic electron-electron repulsion is taken into account by integrating the repulsion term. This gives the average effect of the repulsion, but not the explicit repulsion interaction[32]. This is a variation calculation, meaning that the approximate energies calculated are all equal to or greater than the exact energy. The energies are calculated in units called Hartrees (1 Hartree = 27.2116 eV).

2.3 .3 Density Functional Theory (DFT)

DFT has proven hugely successful in the calculation of structural properties of condensed matter systems and the electronic properties of simple metals[33]. Its advantages include less demanding computational effort, less computer time, and in some cases better agreement with experimental values than is obtained from other procedures. The premise behind DFT is that the energy of a molecule can be determined from the electron density instead of a wave function. The original theorem applied only to finding the ground-state electronic energy of a molecule [30]. DFT focuses on the much simpler electron density $\rho(r)$. In general, the electron density is the number of electrons N per unit volume for a given state. It is dependent only on three coordinates independently of the number of electrons of the system, thus [34]:

$$N = \int \rho(\vec{r})d\vec{r} \quad \dots\dots\dots(2-11)$$

The difference between the methods of density function theory is the method of choosing the shape of function to calculate the energy of bonding and exchange.

2.4 The Hybrid Functional

Another set of functionals that are widely used are the hybrid exchange-correlation functionals. These combine the density function theory (DFT) with Hartree –Fock theory (HF). The most popular hybrid functional B3LYP(Becke's3 parameter exchange correlation functional which uses 3 parameters) and LYP (The Lee, Yang and Parr correlation functional) [27].

2.5 Gaussian 09(G09) Program

One of the famous programs in computational chemistry can work in the operating system Windows and Linux and there are copies of capacities 32 bit and 64 bit. All of the computational calculations were performed using the Gaussian 09 Revision- A.02 SMP suite of program with GUI (Graphical User Interface) called Gauss view, version 5.0.8 (GV5 for short)[35]. Gaussian 03 Revision B.01 with Gauss view 3.07 (GV3 for short) [36]. The '09' and '03' refers to the year 2009 and 2003 respectively, in which the software was published. G09 is the most recent version. G09 contains about 500,000 lines (very approximate) of FORTRAN and C++ code. Initiated by sir John Pople (shared Nobel prize with Walter Kohn in 1998) in the late 1960, the first distributed Gaussian package was labeled Gaussian 70 [37].

2.6 Structural Properties

The arrangement of atoms in the molecules and more specifically the electrons around the atom determine the energy level of that molecule. In fact, the energy of a molecular system varies even with small changes in its structure. This is why geometry is so important when performing calculations. The objective of a geometry optimization is to find the point at which the energy is at a minimum because this is where the molecule is most stable and most likely to be found in nature [38]:

1. Number and types of atoms
2. Number and types of bonds
3. Relevant bond lengths r : $0 \leq r \leq \infty$ (in units of angstroms (Å))

4. Relevant bond angles θ : $0 \leq \theta \leq 180^\circ$ (in units of degrees)
5. Relevant dihedral angles: $-180^\circ \leq \phi \leq 180^\circ$ (an angle between four atoms, which signifies the 3-dimensional shape of the molecule).

Geometry optimization is a standard chemistry-physical calculation to find the lowest energy or largest relaxed conformation for a molecule. The approach is involving an iterative process, at each step, the molecular geometry is modified slightly and the energy of the molecule is compared with the last cycle. The computer moves the molecule a little, calculates the energy, moves it a little more, and keeps going until it finds the lowest energy. This is the minimum energy of the molecule and obtained at the optimized geometry [39,40].

2.7 Electronic Properties

2.7.1 Total Energy, Ionization Potential and Electron Affinity

The total energy for a system is the sum of total kinetic and potential energy, at the optimized structure that the total energy of the molecule must be at the lowest value because the molecule is at the equilibrium point this means that the resultant of the effective forces is zero. The ionization potential (IP) for a molecule is the amount of energy required to remove an electron from an isolated atom or molecule and expressed as the energy difference between the positive charged energy $E_{(+)}$ and the neutral $E_{(n)}$ according to the following relation:

$$IP = E_{(+)} - E_{(n)} \quad \text{.....(2-12)}$$

The electron affinity (EA) of a molecule or atom is the energy change when an electron added to the neutral atom to form a negative ion and expressed as the energy difference between the neutral energy $E_{(n)}$ and the negative charged energy $E_{(-)}$ according to the following relation:

$$EA = E_{(n)} - E_{(-)} \quad \text{.....(2-13)}$$

In molecular orbital (MO) theory within the limitation of Koopmans' theorem [41], the orbital energies of the frontier orbitals are given by:

$$IP = -E_{\text{HOMO}} \quad \text{.....(2-14)}$$

$$EA = -E_{\text{LUMO}} \quad \text{.....(2-15)}$$

Where E_{HOMO} is the energy of highest occupied molecular orbital, and E_{LUMO} is the energy of lowest unoccupied molecular orbital.

2.7.2 HOMO, LUMO and Band Gap

These acronyms stand for the highest occupied molecular orbital (HOMO), and the lowest unoccupied molecular orbital (LUMO). The HOMO is the molecular orbital of highest energy that is occupied by electrons. The LUMO is the molecular orbital of lowest energy that is not occupied by electrons. The HOMO and LUMO are important in determining such properties as molecular reactivity and the ability of a molecule to absorb light [27]. The band gap refers to energy difference between the highest occupied molecular orbital and lowest unoccupied molecular orbital according to the Koopmans' theorem [42]:

$$E_g = E_{\text{LUMO}} - E_{\text{HOMO}} \quad \text{.....(2-16)}$$

HOMO and LUMO and their resulting energy gap not only determine the way the molecule interacts with other species, but their energy gap (frontier orbital gap) helps characterize the chemical reactivity and kinetic stability of the molecule. A molecule with a small frontier orbital gap is more polarizable and is generally associated with a high chemical reactivity, low kinetic stability and is also termed as soft molecule.

2.7 .3 Dipole Moment

molecule possesses a permanent electric dipole moment if its center of positive charge does not coincide with its center of negative charge. The permanent electric dipole moments are often present in neutral molecules for neutral systems, the dipole moment is calculated from the atomic charges and the lone-pairs as:

$$X_i = Ce \sum_A Q_A i_A + 2Cea^0 \sum_A \rho(S - \rho_i)_A D(A)A \quad \dots\dots(2-17)$$

Where $i = x, y, z$, C is speed of light, e is the electron charge, Q_A is total electron density, a_0 is Bohr radius, $\rho(S-\rho_i)$ is one-center $S-\rho_i$ electron density matrix element, and $D(A)$ is the one-center two-electron integral.

The total dipole moment is [43]:

$$X = X_x + X_y + X_z \quad \dots\dots\dots(2-18)$$

2.7 .4 Chemical Potential (κ) and Electronegativity (χ)

The fundamental variation principle in density functional theory is the electronic chemical potential, where the reactivity indicator is related to how the electronic energy E of a molecule changes with changing the number of electrons N and the external potential. Parr *et al.* showed that for every collection of nuclei and electrons system there was electronic

chemical potential K , defined as [44]:

$$K = \left[\frac{\partial E}{\partial N} \right]_V \quad \dots\dots\dots(2-19)$$

Where v is the potential due to nuclei.

Then we might define the electronegativity (it is defined as “the power of an atom in a molecule to attract electrons to itself by Pauling) as the negative of the electronic chemical potential [45]:

$$X = -K = - \left[\frac{\partial E}{\partial N} \right]_V \quad \dots\dots\dots(2-20)$$

R. Mulliken defined electronegativity as the average of the ionization energy and electron affinity as follows[46]:

$$X = \frac{(IP+EA)}{2} \quad \dots\dots\dots(2-21)$$

According to Koopmans’ theorem, it can be defined as the negative value for average of the energy levels of the HOMO and LUMO [27,47]:

$$X = - \frac{(E_{HOMO} + E_{LUMO})}{2} \quad \dots\dots\dots(2-22)$$

2.7 .5 Chemical Hardness (η) and Chemical Softness (S)

The chemical hardness (η) is a measure of the resistance to charge transfer. The theoretical definition of chemical hardness has been provided by the density functional theory as the second derivative of electronic energy with respect to the number of electrons N , for a constant external potential $V(r)$ [48]:

$$\eta = \frac{1}{2} \left[\frac{\partial^2 E}{\partial N^2} \right]_V = \frac{1}{2} \left[\frac{\partial K}{\partial N} \right]_V = - \frac{1}{2} \left[\frac{\partial X}{\partial N} \right]_V \quad \dots\dots\dots(2-23)$$

Finite difference approximation to chemical hardness gives,

$$\eta = \frac{IP-EA}{2} \quad \dots(2-24)$$

The hard molecule has a large energy gap and the soft molecule has a small energy gap. In quantum theory, changes in the electron density of system result from the mixing of suitable excited state wave functions with the ground state wave function. A small energy gap means small excitation energies to the manifold of excited states. Therefore, soft molecules with small energy gaps. Their electron density change more easily than a hard molecule, and due to that, soft molecules will be more reactive than hard molecules [41].

The global chemical softness, S , is a property of molecules that measures the extent of chemical reactivity. It is the inverse of the chemical hardness (η)[49]:

$$S = \frac{1}{2\eta} = \left[\frac{\partial^2 N}{\partial E^2} \right]_V = \left[\frac{\partial N}{\partial K} \right]_V \quad \dots\dots\dots(2-25)$$

2.7.6 Electrophilicity (ω)

The Electrophilicity is definition as an index measures the stabilization in energy when the system acquires an additional electronic charge from the environment [42]. On the other word, it can be defined as a measure of energy lowering due to maximal electron flow between donor and acceptor[49].

$$\omega = \frac{\kappa^2}{2\eta} \quad \dots\dots\dots(2-26)$$

Where κ chemical potential is associated with the negative of the electronegativity

2.7.7 Cohesive Energy (E_{coh})

Cohesive energy is defined as the energy required to separating the condensed material into isolated free atoms. The cohesive energy is then the difference between energy per atom of the bulk material at equilibrium and the energy of a free atom in its ground state. To calculate this propriety it is required the value of the total energy of the system (molecule) and of the free atoms. The cohesive energy E_{coh} is given by [50]:

$$E_{coh} = (E_{tot} / n) - E_{free} - E_0 \quad \dots\dots\dots(2-27)$$

Where E_{tot} is the total energy. E_{free} is the free atoms *sp* shell energy, n is the number of atoms, E_0 is the vibration energy of ground states (zero-point). The energy difference between atoms and a molecule is a measure of the bonding strength for the system molecule. It is possible to derive the law from the definition of binding energy “The cohesive energy is the energy difference between molecules”.

CHAPTER THREE

RESULTS AND DISCUSSION

3.1 Introduction

This chapter includes the results and discussion of structural for (PVA- Al_2O_3) nanocomposites. Effect of addition the Al_2O_3 nanoparticles on structure and electronic properties of (PVA- Al_2O_3) nanocomposites are discussed in this chapter.

Gaussian view 5.0 program and density functional theory (DFT) are used to calculate many properties. The properties were investigate total energy, energy gap, LUMO, HOMO, cohesive energy, density of states, ionization potential, electron affinity, chemical hardness, chemical softness, electronegativity. Also, the spectroscopic properties (IR , UV-Vis , RAMAN) for (PVA- Al_2O_3). Density functional theory (DFT) at the generalized gradient approximation level of local spin density approximation (LSDA) with *LanL2DZ* basis sets are used. Geometrical optimization is performed first and followed by electronic properties, frequency and vibrational analysis.

3 .2 The Structural Properties and Geometry of (PVA- Al_2O_3) Nanocomposite

The geometrical optimization of nanocomposites was theoretical calculated. It's determines many of its physical and chemical properties. It is necessary to find the relaxation of the nanocomposites, in which the optimized structure of the nanocomposite is the structure a minimum energy. Figure (3.1) _ (3.2) shows the optimized structures of (PVA) (43Atoms) and (PVA- Al_2O_3)(48Atoms) nanocomposites in the gas state, were obtained with the DFT method using the three-parameter hybrid-functional of Becke (B3LYP) with (*LanL2DZ*) basis sets.

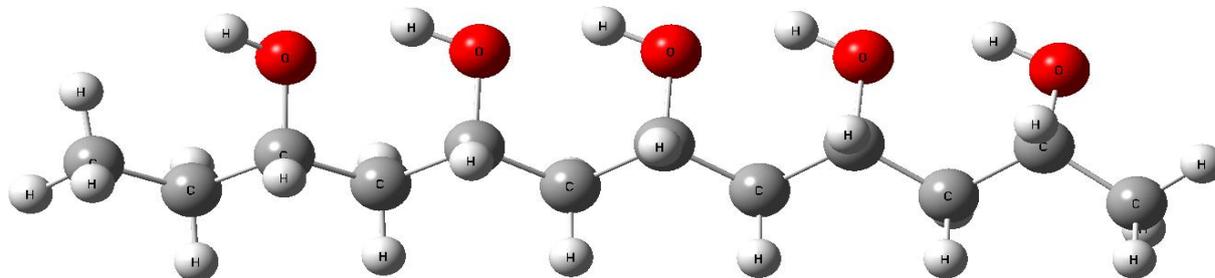


Fig. (3.1). Optimized geometry for (PVA) contain (43 Atoms) at the *B3LYP/LanL2DZ* basis set.

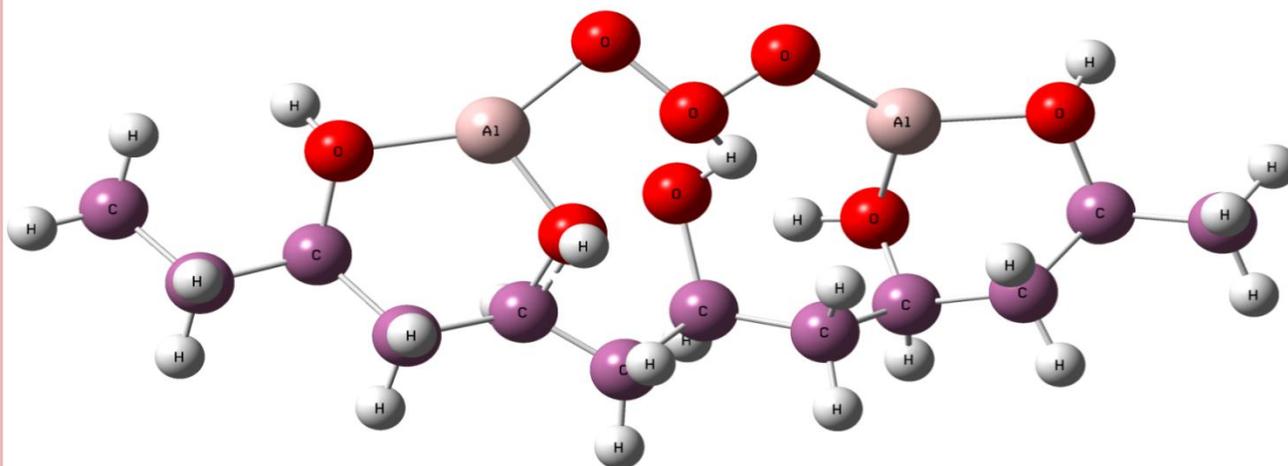


Fig. (3.2). Optimized geometry for (PVA- Al_2O_3) contain (48 Atoms) at the *B3LYP/LanL2DZ* basis set.

Table (3.1) shows the geometric parameters of (PVA-Al₂O₃) nanocomposite involved the bond length in Angstrom and bond angle in degree by using the Gaussian 09 package of programs by employing the DFT with the B3LYP/ *LanL2DZ* level. It has been deduced that the DFT method is an efficient to estimate the optimized structure of the studied molecule, that due to the DFT method characterized by its accuracy to estimate the molecular properties for any compound. The calculated values of bonds in present work are in a good agreement with previous theoretical studies [51,52].

Table (3.1). Average bond lengths in (Å) and in degree

Measurements	The optimization parameters	Values
Bonds Å	(C-C)	1.542
	(C-O)	1.480
	(C-H)	1.096
	(O-H)	0.994
	(O-O)	1.573
	(Al-O)	1.912
Angles Deg.	(C-C-C)	114.884
	(C-O-H)	108.623
	(O-Al-O)	73.976

3.2.1 Fourier Transform Infrared Radiation (FTIR) of Nanocomposite

FTIR spectra of (PVA-Al₂O₃) nanocomposite are shown in Figures (3.3)_ (3.4). The FTIR studies of nanocomposites show the interactions in nanocomposites. It has been found that the strong peak observed at (3299 cm⁻¹) is attributed to the (O-H) groups. The results obtained using the Gaussian view 5.0 program and density functional theory (DFT) with (*LanL2DZ*) basis sets. Table (3.2) shows the values of FTIR calculated which we observe through it.

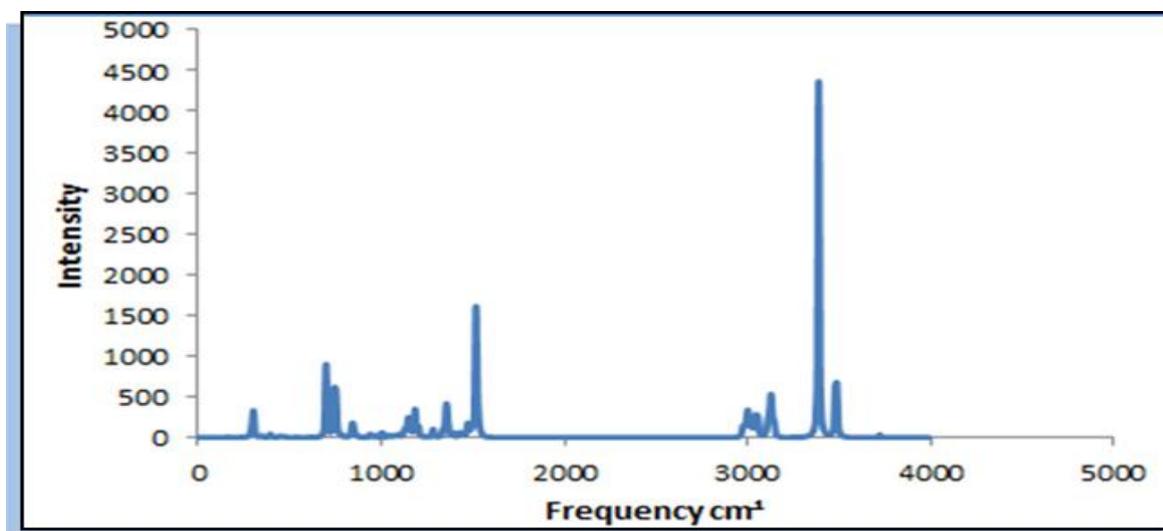


Fig. (3.3). IR spectrum of (PVA) (43Atom) using *B3LYP/LanL2DZ*.

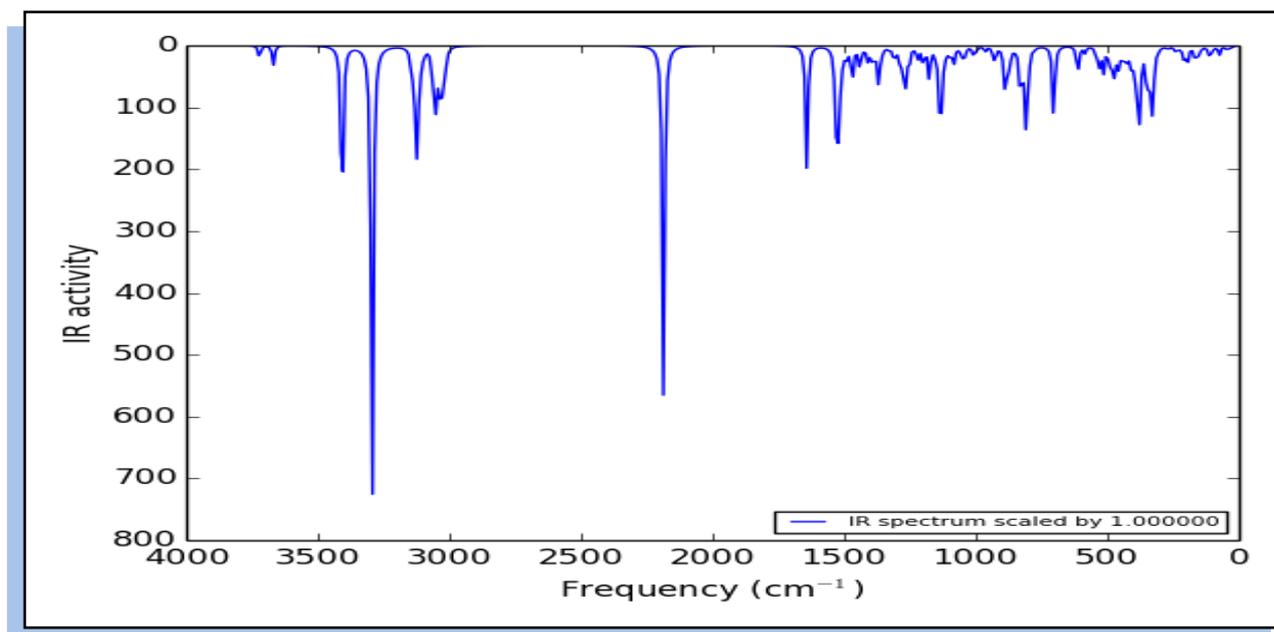


Fig.(3.4).IR spectrum of(PVA- Al_2O_3) (48 Atoms).

Table (3.2). IR frequencies with their assignments of (PVA- Al_2O_3) obtained by DFT using B3LYP/ *LanL2DZ* basis set.

Assignment	Type of vibrational mode	Frequency (cm^{-1})	Typical vibrational frequency (cm^{-1})
Al-O	Symmetric stretching	400-600	500-650
C-O	Stretching and bending	1085.52	1000-1280
-CH ₃	in-plane bending	1413.73	841-1420
C-H	Stretching	2906.97	2900-3100
O-H	Symmetric stretching	3215.24	3200-3600

The differences between a Raman spectrum and an infrared spectrum are not surprising. Infrared absorption requires that a vibrational mode of the molecule have a change in dipole moment or charge distribution associated with it. However, Raman intensities are more difficult to compute in comparison with IR intensities, as a mixed third derivative is required to approximate the change in the molecular polarizability with respect to the vibration that is computed. Raman is a very powerful tool for analysis and chemical monitoring. Figures (3.5) - (3.6) show the Raman spectrum of (PVA) (43Atoms),(PVA- Al_2O_3) (48Atoms. It shows from the figures that the active region in IR is similar with less activity in Raman . The peak intensities in Raman spectrum

depend on the probability that a particular wavelength photon will be absorbed. These probabilities can be computed from the wave function by computing the transition dipole moments. This gives relative peak intensities since the calculation does not include the density of the substance. Some types of transitions turn out to have a zero probability due to the molecules' symmetry or the spin of the electrons.

Raman and FTIR are complementary vibrational spectroscopic techniques. In Raman spectroscopy, a change is observed in the polarization of molecules; that is, a visible or ultraviolet photons interacts with the vibrating molecular bonds, gaining or losing part of their energy, thereby generating the spectrum. An advantage of Raman spectroscopy is that the spectral analysis is carried out in reflection mode, so tissues can be probed in their native state without any, or minimal preparation [53]. The active region is take place in the range about (1000-4000) cm^{-1} in all nanocomposites. From figures show the specific bands of nanocomposites appear with their original characteristics. No significant change or shift of them could be observed.

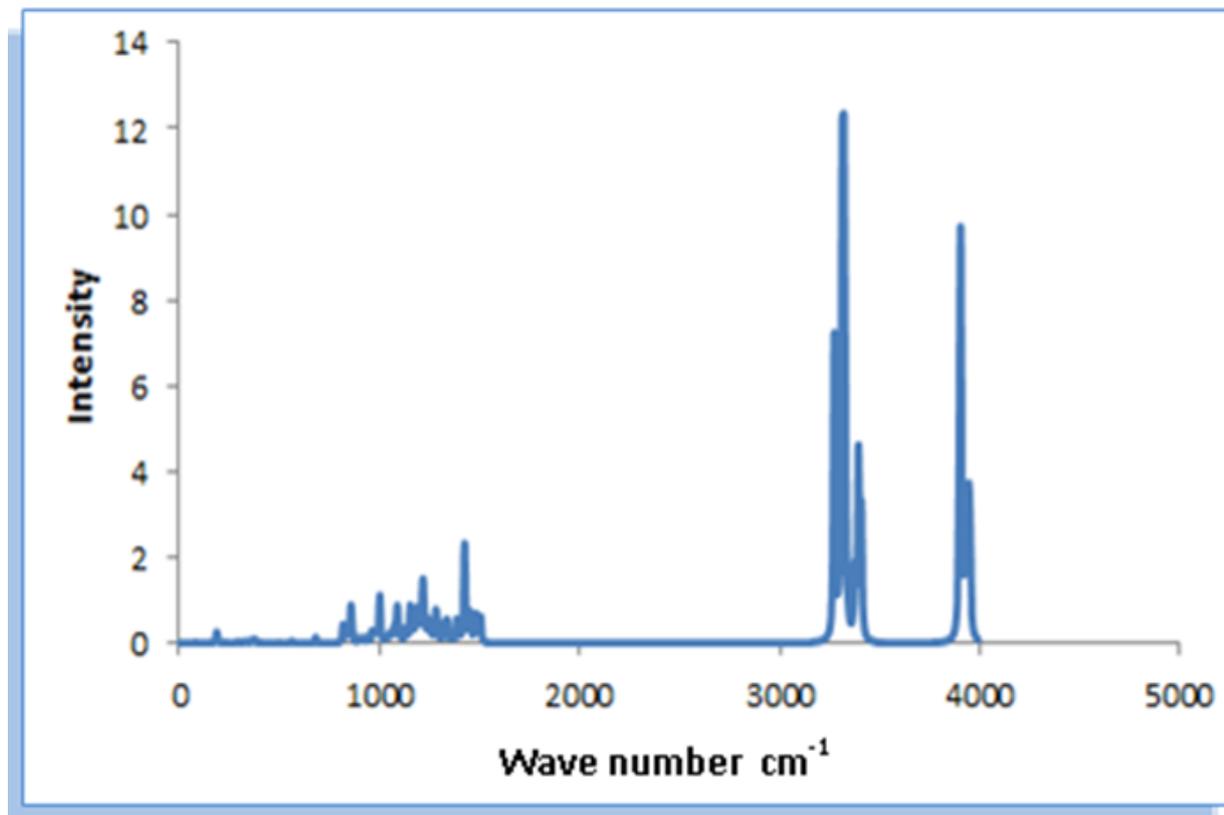


Fig. (3.5'). Raman intensities of (PVA) (43Atoms).

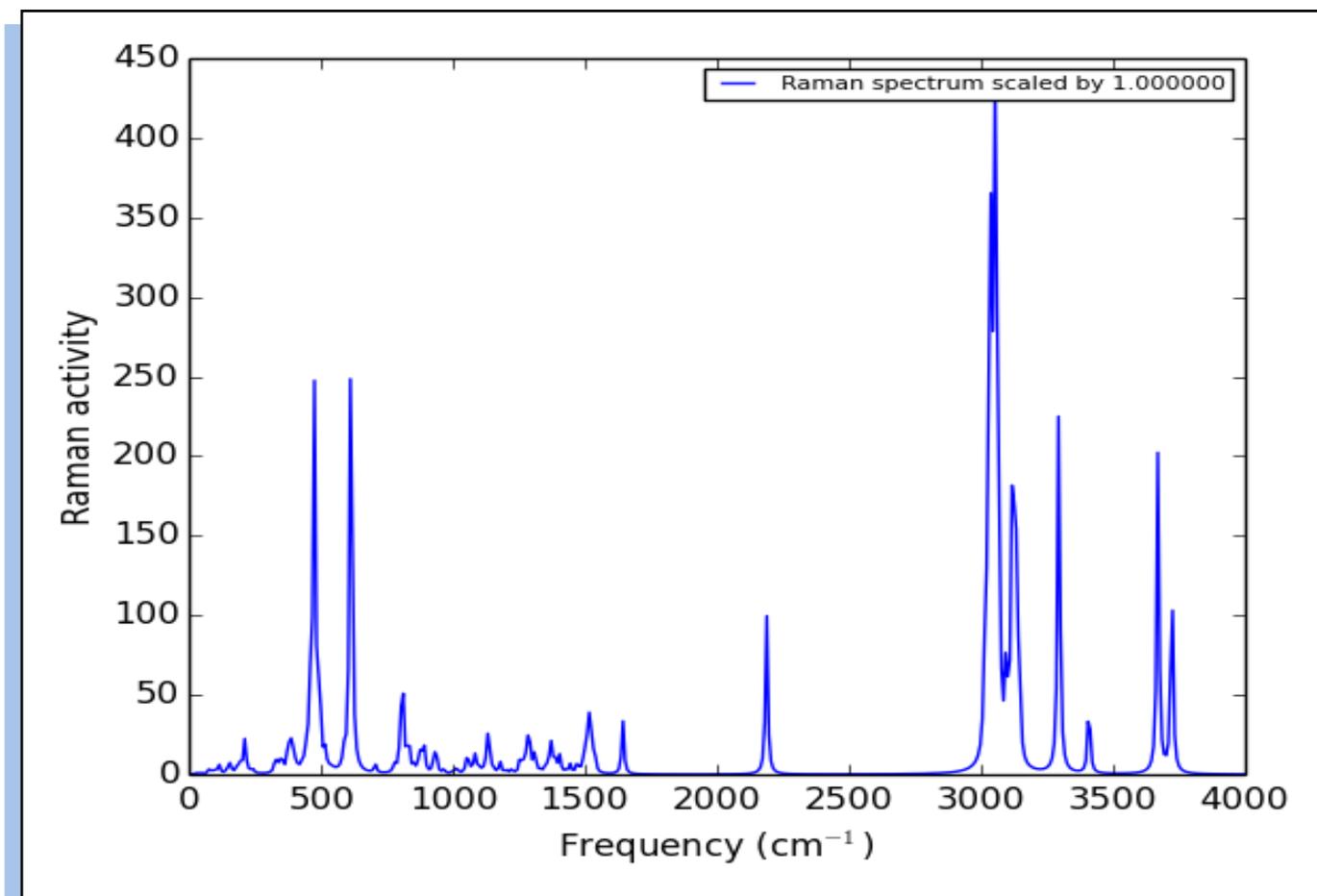


Fig. (3.6). Raman intensities of (PVA- Al₂O₃) (48Atoms).

3.2.3 Nuclear Magnetic Resonance (NMR)

Chemical shifts of the structure were calculated at the same level using the Gauge-Included Atomic Orbital (GIAO) approach. Gauge-Independent Atomic Orbital (GIAO) method is used in the present NMR calculations. Absolute isotropic magnetic shielding were transformed into chemical shifts by referencing to the shielding of a standard compound (TMS) computed at the same level. The chemical shifts were reported in (ppm) relative to (TMS) for ^1H spectra as shown in Figures (3.7)-(3.8).

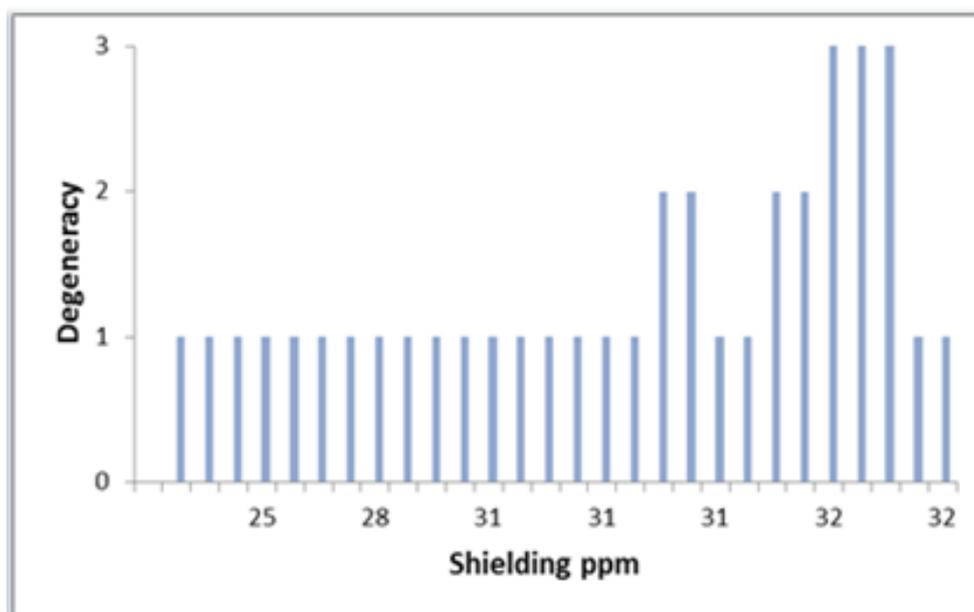


Fig. (3.7). Nuclear Magnetic Resonance of (PVA) (43 Atoms).

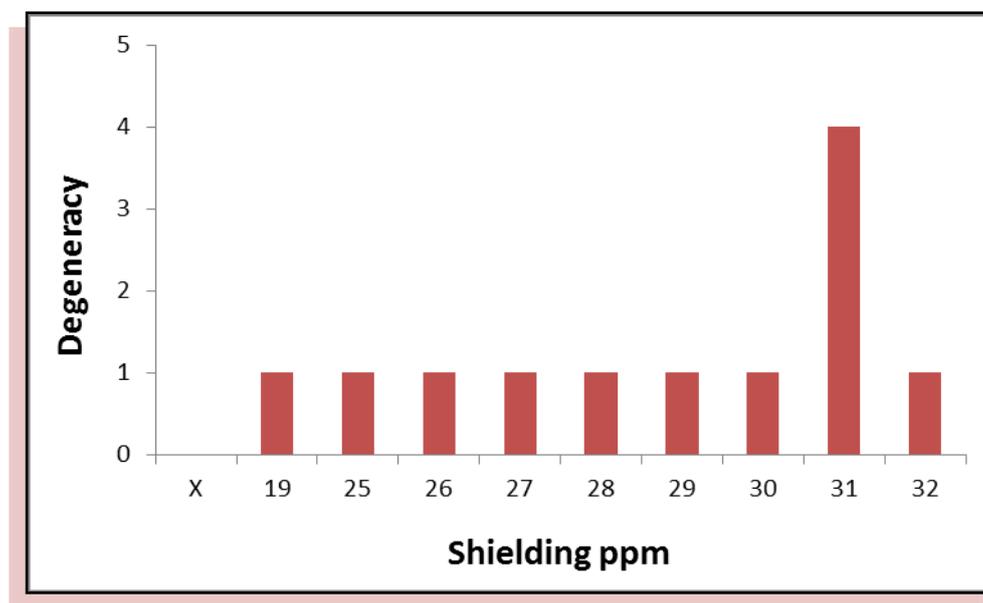


Fig. (3.8). Nuclear Magnetic Resonance of (PVA- Al_2O_3) (48 Atoms).

3.3 The Effective Resulting Energies of (PVA- Al_2O_3) Nanocomposite

The electronic properties of structures, Table (3.3) demonstrate the energies, cohesive energy (E_{coh}), ionization potential (IP), electron affinity (EA), electronegativity (EN), electrophilicity (ω) for these structures. Present work are in a good agreement with previous theoretical studies [54].

Table (3.3) The values of some electronic properties in eV of the studied structures.

Property	PVA 43 Atoms	(PVA-Al₂O₃) 48 Atoms
<i>Total energy</i>	- 23101.333 (a.u)	-1559.414 (a.u)
<i>Ionization potential</i>	5.933	3.960
<i>Electron affinity</i>	-0.922	0.477
<i>Electronegativity</i>	2.505	2.218
<i>Chemical hardness</i>	3.428	1.741
<i>Chemical softness</i>	0.1458	0.287
<i>Chemical potential</i>	-2.505	- 2.218
<i>Electrophilicity</i>	0.915	1.412
<i>Dipole moment (Debye)</i>	13.569	13.388
<i>Polarizability (a.u)</i>	144.647	242.751

The computed total energy E_T data shown in table (3.3) suggest that it increase (in magnitude) with increase in the number of atoms for all studied nanocomposites. It is well known that the frontier molecular orbitals, the highest occupied molecular orbital HOMO and the lowest unoccupied molecular orbital LUMO, play a significant role for the reactant molecules in chemical reactions. The hard molecule has a large energy gap and the soft molecule has a small energy gap. In quantum theory, changes in the electron density of system result from the mixing

of suitable excited state wave functions with the ground state wave function. A small energy gap means small excitation energies to the manifold of excited states. Therefore, soft molecules with small energy gaps, their electron density change more easily than a hard molecule, and due to that, soft molecules will be more reactive than hard molecules. The experimental conditions (impurities, grain size, reaction atmosphere, and synthesis conditions) play a relevant role on the energetic determination [54]. The lowering IP is the factor for the nanocomposites to donating an electron and the large value of EA is the factor for determining the high ability to accepting an electron. Low values of hardness H indicates easily to an electron transfer from valance to conduction band, and this is a reflection to small band gap that the nanocomposites have.

The high values of chemical softness S means that the nanocomposites need small excitation energy for an electron transfer and small energy gap it have. The nanocomposites which have high values of polarizability will be more effective, less stable, more softness and have small energy gap.

3.4.1 The Absorbance of (PVA- Al_2O_3) Nanocomposite

Ultra Violet and Visible spectrum is dependent upon the electronic structure of the molecule. Figures (3.9)-(3.10) Shows the UV-Vis spectra that obtained by using Gaussian 09 program and Gaussian view 5.0.8 program and using density functional theory (DFT) at *B3LYP* level with

LanL2DZ basis sets. The figures show that the spectrum within the limits Ultraviolet-Visible (UV-Vis) of the spectrum, because the rate of spectrum is taken to concentrations. Which, will calculate the highest concentration where the sample will be completely opaque only seen in the visible area of the spectrum and at a lower concentration which will be in the Ultra Violet area of the spectrum.

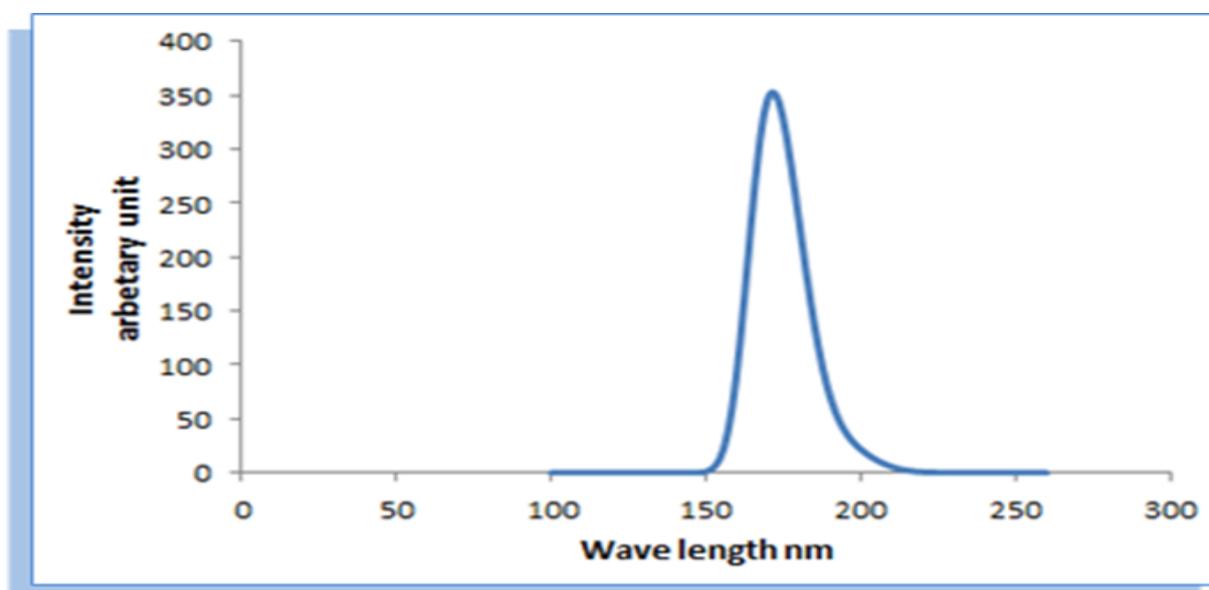


Fig. (3.9). UV-Vis spectrum for (PVA) (43 Atoms) .

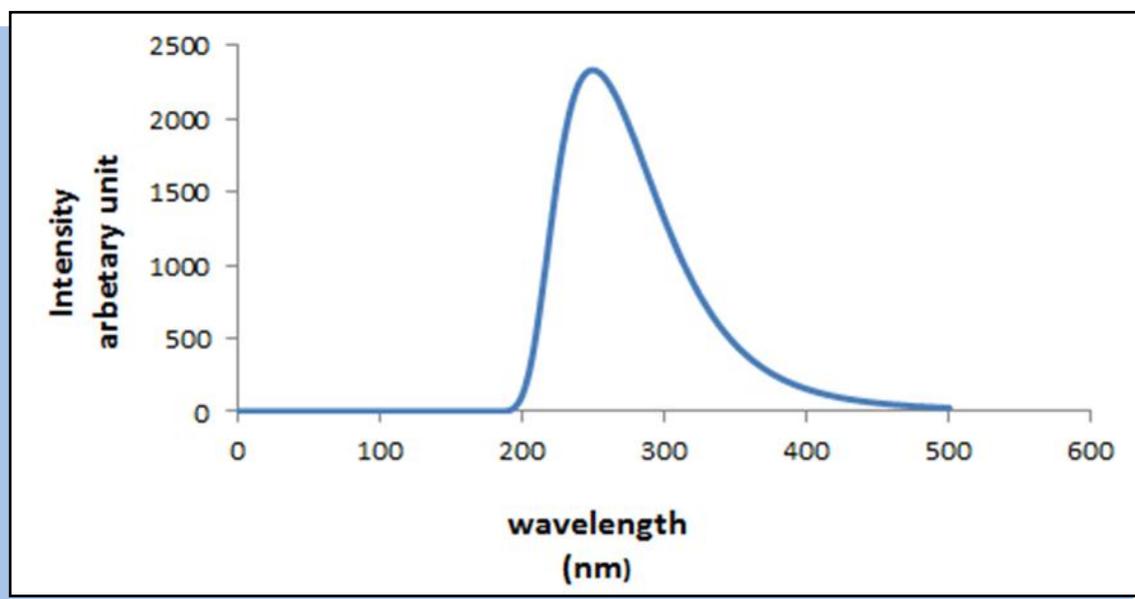


Fig. (3.10). UV-Vis spectrum for (PVA- Al₂O₃) (48 Atoms) .

3.4.2 The Energy Band Gap of (PVA- Al₂O₃) Nanocomposite

The energy band gap found by using equation (2-16). The band gap refers to energy difference between the highest occupied molecular orbital and lowest unoccupied molecular orbital according to the Koopmans' theorem. Table (3.4) shows the energy gap for nanocomposites (PVA) (43Atoms) , (PVA- Al₂O₃) (48Atoms).

Figures (3.11)_ (3.12) shows the 3-D distribution of HOMOs and LUMOs for the studied nanocomposites.

From these figures, the form of the nanocomposites have same an effect on both HOMO and LUMO distribution. The change of the form of

the nanocomposites leads to change the map of HOMO and LUMO distribution according to the linear combination of atomic orbitals-molecular orbital LCAOs-MO.

Table (3.4) . The values of energy gap in (eV) of the studied structures

PVA 43 Atoms			PVA-Al ₂ O ₃ 48 Atoms		
E _{HOMO} (eV)	E _{LUMO} (eV)	E _g (eV)	E _{HOMO} (eV)	E _{LUMO} (eV)	E _g (eV)
-5.933	0.922	6.856	-3.960	-0.477	3.483

The addition of (Al₂O₃) nanoparticles to (PVA) led to a reduction of the energy gap from (6.8568)eV to (3.483)eV. These results in present work are in a good agreement with previous theoretical studies[54,52].

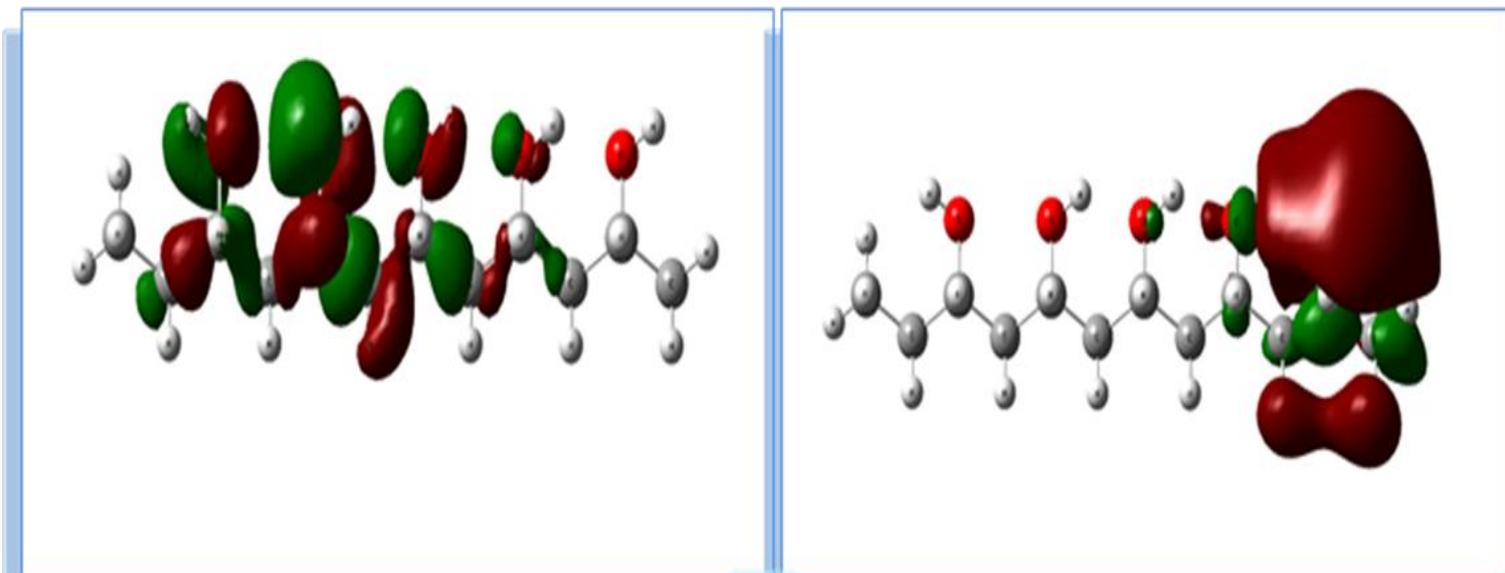


Fig. (3.11). The distribution of HOMO (left) and LUMO (right) for
(PVA) (43 Atoms).

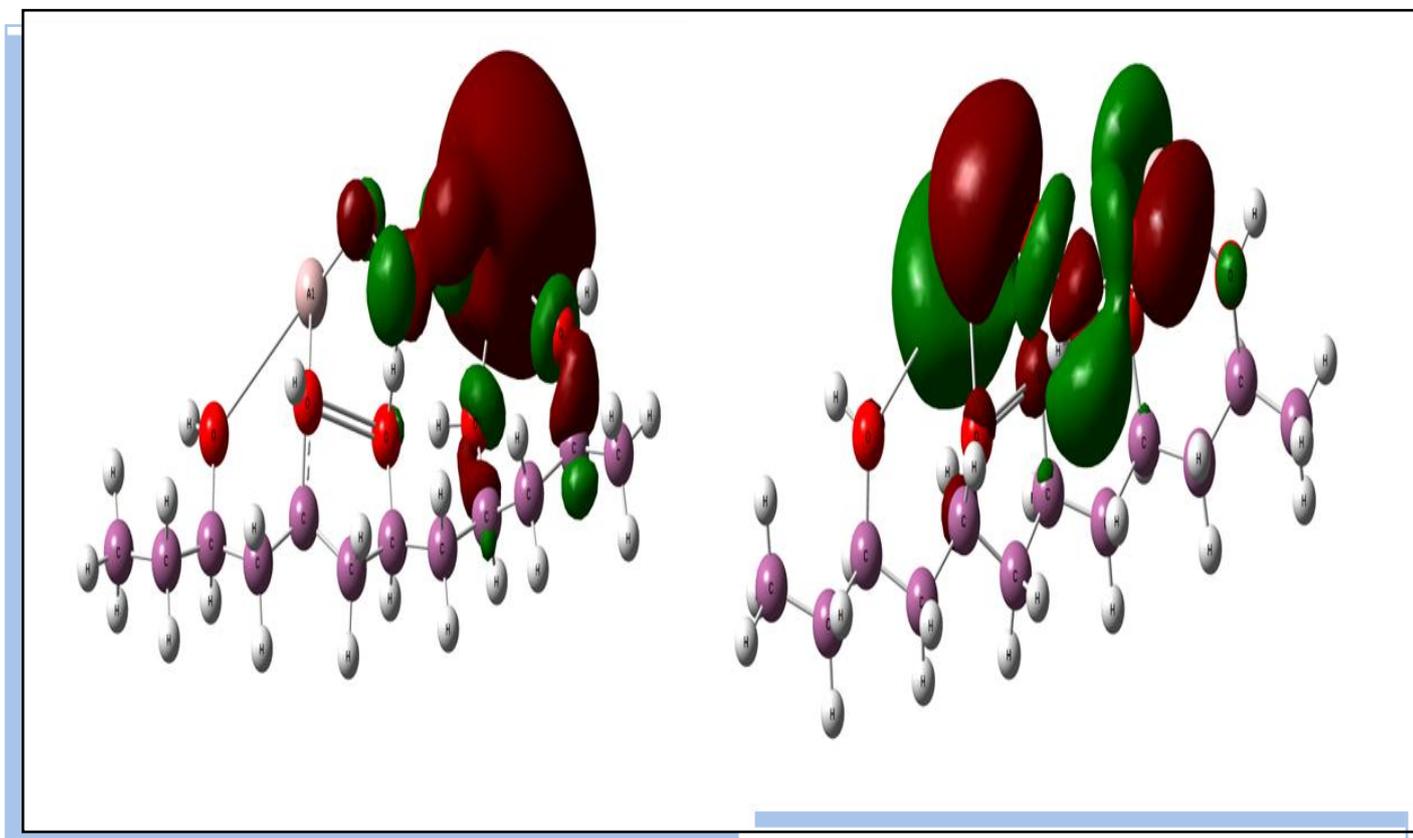


Fig. (3.12). The distribution of HOMO (left) and LUMO (right) for (PVA- Al₂O₃) (48 Atoms).

3.4.3 Density of States

The strength of interactions can be further studied by analyzing orbital interactions between the atoms of nanocomposite, in terms of density of states DOS as shown in Figures (3.13) - (3.14). The DOS governs many physical properties and consequently plays an important role in solid state physics, it is important to be able to predict how the DOS will behave for different molecular structures geometries. The degeneracies

of unoccupied molecular orbitals are more than the occupied molecular orbitals. The high density of states at a specific energy levels refers to that there are many states in the structure available for occupation. If there is no states can be occupied at that energy level that refers to zero density of states. The theoretical and measurements calculations indicate that the direction of electron transfer is from transition metal to carbon and due to the increase in their electronegativity. The metal lattice expands and the metal–metal distance increases upon carbide formation, the increase in metal–metal distance causes contraction of the metal d-band and therefore would give a greater density of states (DOS) near the Fermi level [55].

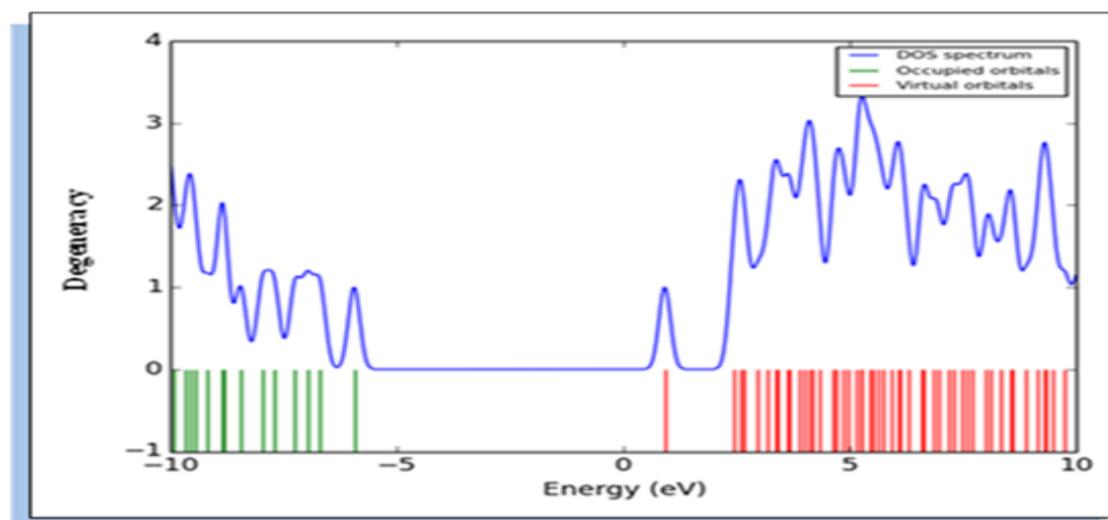


Fig. (3.13). The density of states as a function of energy for
(PVA)(43 Atoms).

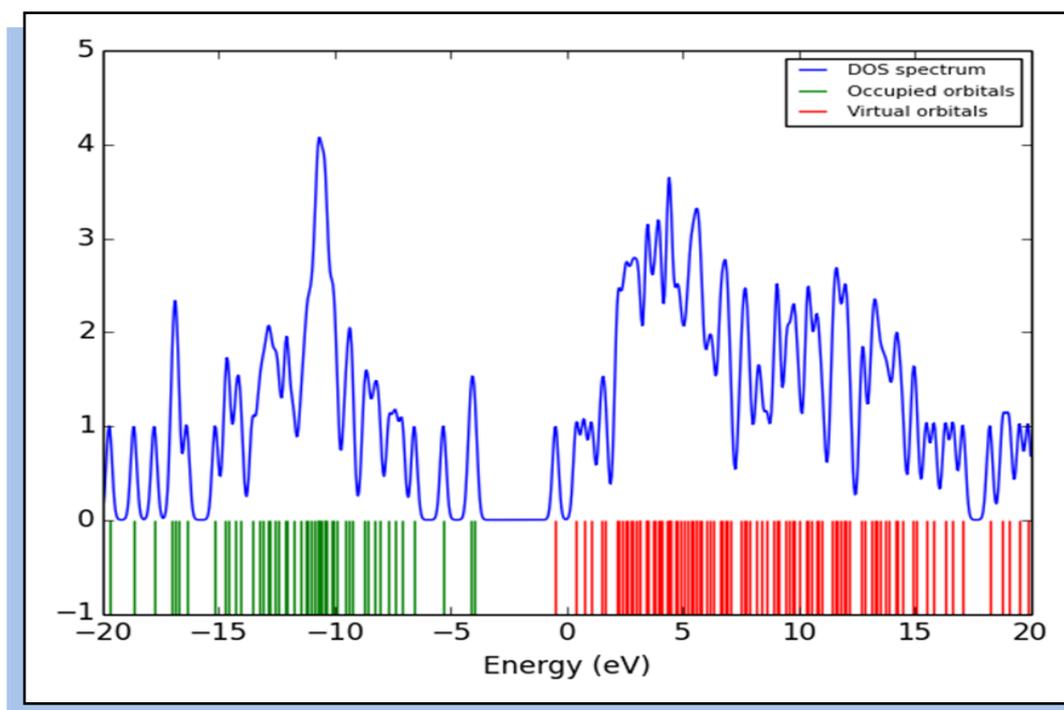


Fig. (3.14). The density of states as a function of energy for
(PVA- Al₂O₃)(48Atoms).

3.4.4 Electrostatic Potential of (PVA- Al₂O₃) Nanocomposite

Figures (3.15) - (3.16) show the electrostatic potential ESP distribution surface of nanocomposites calculated from the total self-consistent field SCF. The ESP distributions for the nanocomposites in results from the strength of repulsion or attraction of the areas that surrounding each nanocomposites. In general, the ESP surfaces of the (PVA) , (PVA- Al₂O₃) nanocomposite are dragged toward the positions of negative charges in each molecule means the oxygen atoms

of high electronegativity[3.5 eV].

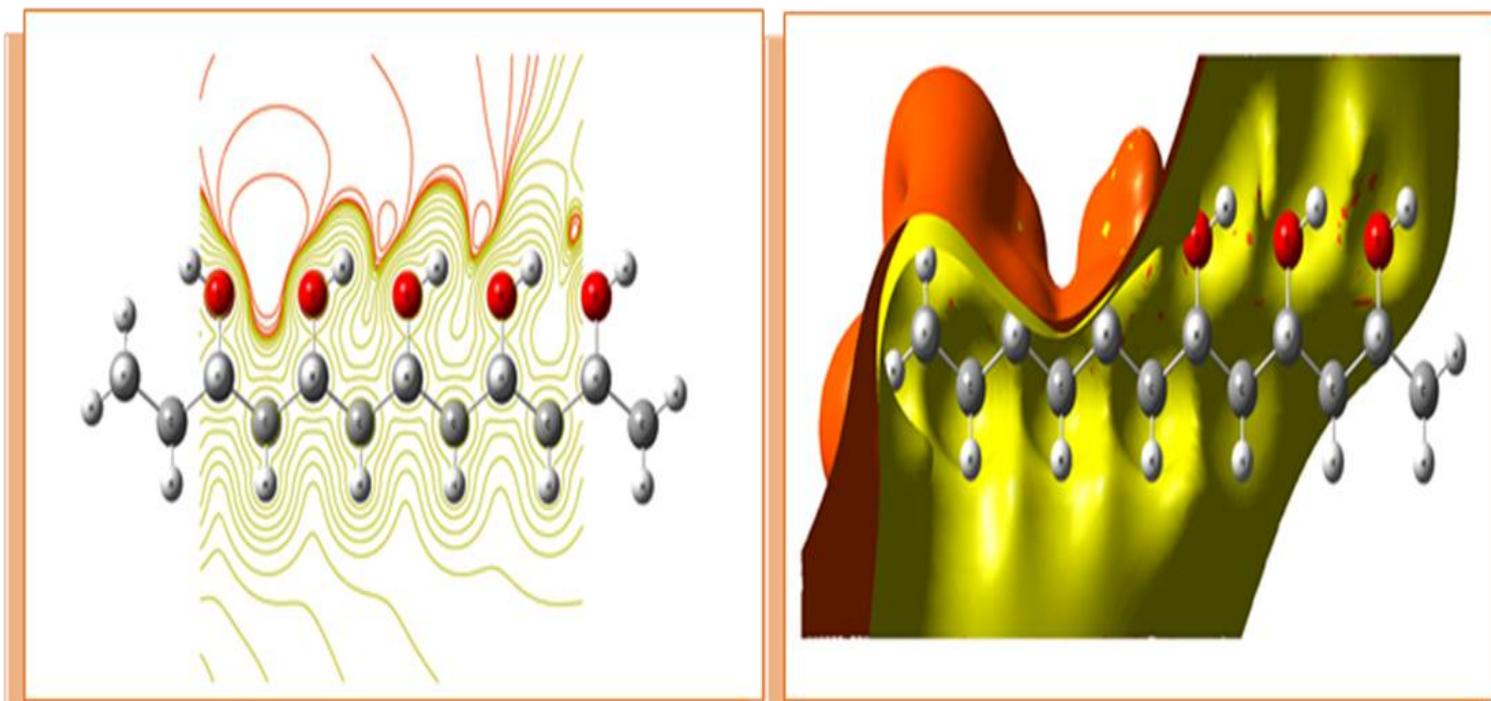


Fig. (3.15). The electrostatic potential distribution surface for
(PVA)(43 Atoms) (left: 2-D counter; right: 3-D).

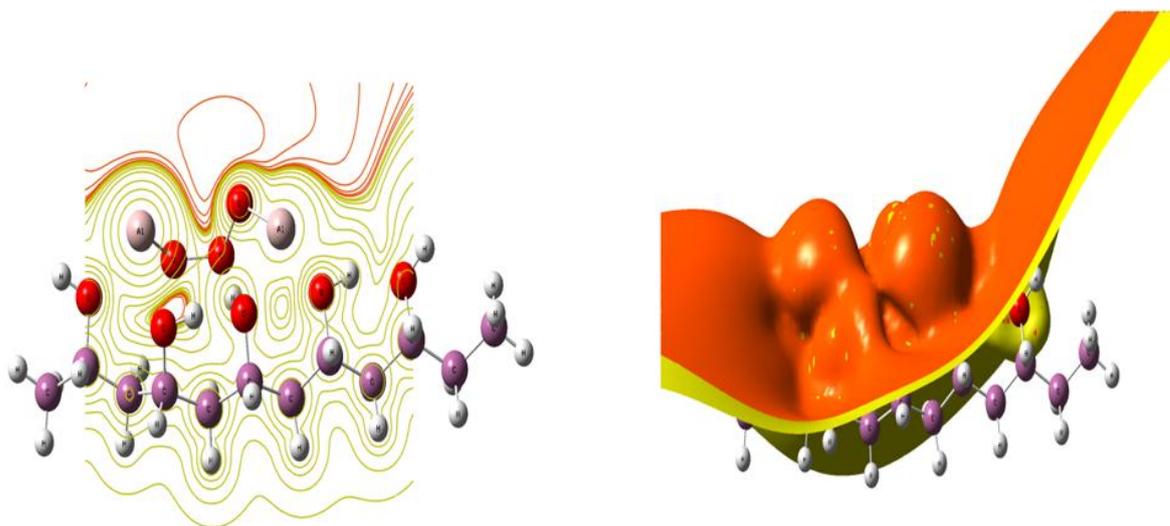


Fig. (3.16). The electrostatic potential distribution surface for (PVA- Al₂O₃)(48 Atoms) (left: 2-D counter; right: 3-D).

CHAPTER FOUR

CONCLUSIONS AND FUTURE WORK

4.1 Conclusions

- 1- The stability decreasing when an addition Al_2O_3 nanoparticles, because increasing the total energy.
- 2- One of the important results obtain in this study, is the decreasing of the energy gap. This declares that these nanocomposites are the nearest to semiconductor because the both HOMO and LUMO levels become more adjacent.
- 3- PVA need small energy to become cation because ionization potential is decrease with an addition Al_2O_3 nanoparticles.
- 4- The hardness decrease with an addition Al_2O_3 nanoparticles, therefore all the nanocomposites are softer, and this reduces the resistance of a species to lose electrons.
- 5- According to the high of the electrophilicity, the $(\text{PVA}-\text{Al}_2\text{O}_3)$ composites are more reactive.
- 6- The results of the properties of singly occupied MO on $(\text{PVA}-\text{Al}_2\text{O}_3)$ showed that can be the key component for the catalytic activities of the alumina .
- 7- Applied in electronics and semiconductor fields .

4.2 Future Work

1. Study of mechanical properties of $(\text{PVA}-\text{Al}_2\text{O}_3)$ nanocomposites.
2. Studying the thermal properties of $(\text{PVA}-\text{Al}_2\text{O}_3)$ nanocomposites.
3. The effect of Al_2O_3 on electrical properties of PVA.
4. Testing the $(\text{PVA}-\text{Al}_2\text{O}_3)$ nanocomposites for humidity sensors.

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الخلاصة

تمت دراسة تأثير إضافة الجسيمات النانوية (Al_2O_3) على الخصائص الهندسية و الالكترونية والطيفية للبوليمر (PVA)(43 Atom) باستخدام برنامج Gaussian 0.9 وبمساعدة Gaussian View 0.5 باستخدام نظرية دالة الكثافة (DFT) مع التقريب (LSDA) ضمن مجموعة الأساس *LanL2DZ*. اشتملت الخصائص الهندسية على تحسين الأمثلية الهندسية (الواصر والزوايا). اما بالنسبة للخصائص الالكترونية فقد تضمنت (الجهود الايوني ، الالفة الالكترونية ، الصلادة، المرونة ، الكهروسالبية ، الطاقة الكلية ، فجوة الطاقة وكثافة الحالات)، وكذلك الخواص الطيفية التي اشتملت على (الأشعة تحت الحمراء(IR)، رامان، الطيف المرئي من الأشعة فوق البنفسجية (UV-visible) والرنين النووي المغناطيسي (NMR)). وقد اتضح من النتائج أن إضافة الجسيمات النانوية (Al_2O_3) له تأثير مباشر على جميع خصائص الجزيئات المدروسة. حيث تؤدي إضافة الجسيمات النانوية (Al_2O_3) إلى انخفاض فجوة الطاقة من (6.856 eV) إلى (3.483 eV) وكذلك الحال بالنسبة إلى معدل طاقة الربط حيث لوحظ انخفاض قيمها مع زيادة عدد الذرات للمتراكبات النانوية التي شملتها الدراسة .

فجوة الطاقة الصغيرة تعني طاقات الإثارة الصغيرة للحالات المتعددة المثارة. لذلك ، الجزيئات اللينة ذات فجوات الطاقة الصغيرة ، تتغير كثافة إلكتروناتها بسهولة أكبر من الجزيئات الصلبة ، ونتيجة لذلك ، ستكون الجزيئات اللينة أكثر تفاعلاً من الجزيئات الصلبة.



جمهورية العراق

وزارة التعليم العالي والبحث العلمي

جامعة بابل

كلية التربية للعلوم الصرفة

قسم الفيزياء المواد وتطبيقاتها

دراسة نظرية للخصائص التركيبية و الالكترونية للمترابك النانوي PVA/Al₂O₃ باستخدام نظرية الدالة الوظيفية

رسالة مقدمة إلى مجلس كلية تربية للعلوم الصرفة - جامعة بابل

وهي جزء من متطلبات نيل درجة الدبلوم العالي تربية / الفيزياء المواد وتطبيقاتها

من قبل

ضحى نعمه صليبي هادي

بكالوريوس علوم فيزياء الليزر (٢٠١٧)

بإشراف

أ.م.د هند أحمد محمد رؤوف

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